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㉓ Use of a composition for the manufacture of a primer for coating dentin.

㉔ Use of an acid and a water-soluble, polymerizable film former, for the manufacture of a polymerizable primer for coating dentin, wherein the acid and the film former are for application sequentially, said acid being applied before said film former, said acid having a pK_a less than or equal to that of phenol, said acid being rinsed from dentin and having a calcium salt which is soluble to form a homogeneous solution in water, said acid having a calcium salt which is insoluble in said film former, said film former being free of adhesively detrimental quantities of calcium salts that are not soluble in said film former.

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Details of Parent Application

The parent application to this divisional application is European Patent Application No. 87301657.0 filed on 25th February, 1987.

Said parent application is limited by virtue of claim 2 thereof in all designated States to use of an acid and a water soluble, polymerizable film former, for the manufacture of a primer for coating dentin, said acid having a pK_a less than or equal to that of phenol, and said acid and its calcium salt(s) being soluble in said film former, said mixture being free of adhesively detrimental quantities of calcium salts that are not soluble in said film former.

By virtue of claim 3 of said parent, which depends from said claim 2 of said parent, it is provided that the acid and the film former can be applied concurrently. Nevertheless there is one particularly preferred embodiment of the invention which is not expressly claimed in said parent application but which forms the subject matter of this divisional application.

In summary, this divisional application covers uses of acids which are disclosed but not claimed in the parent application where the calcium salts of the acids are soluble in water but are not soluble in said film former.

Background Art

In recent years there has been intense interest in the dental field in adhesives that bond to hard tissues such as dentin. Many of these adhesives have been used in conjunction with an acid pretreatment of the dentin prior to application of the adhesive. A very wide variety of acids have been tried, with phosphoric, citric and oxalic acids being particularly popular pretreatments. The use of such acids, especially phosphoric acid, has not been without controversy. The American Dental Association has recommended against phosphoric acid pretreatment of dentin. However, phosphoric acid is extensively used as a pretreatment in Japan in conjunction with dentin adhesives from Kuraray Company, Ltd. Citric acid has a less severe etching effect than phosphoric acid and is used as a dentin pretreatment in the U.S. in conjunction with a dentin adhesive sold by Den-Mat Corporation. Oxalic acid also has a less severe etching effect than phosphoric acid, and the use of its monoacid and certain of its salts as a pretreatment is described in U.S. Patent No. 4,538,990. Other references describing various pretreatments for dentin include M. Buonocore, W. Wileman, and F. Brudevold, J. Dent. Res., 35, 846 (1956), M. Buonocore and M. Quigley, J. Amer. Dent. Assoc., 57, 807 (1958), Public Health Service Publication No. 1494, "Adhesive

Restorative Dental Materials - II", pp. 103-155 (1966), M. Buonocore, "The Challenge of Bonding to Dentin", The Acid Etch Technique, (St. Paul, 1974), N. Nakabayashi, K. Kojima, and E. Masuhara, J. Bio. Mat. Res., 16, 265-273 (1982), K.

Nagata, T. F. Lundeen, and P. T. Turner, J. Bio. Mat. Res., 18, 1089-1103 (1984), R. L. Bowen, R. L. Blosser, and A. D. Johnston, Abstract No. 915, p. 276, AIDR/AADR Abstracts 1985 (Paper presented March 22, 1985), E. C. Munksgaard and E. Asmussen, J. Dent. Res., 63, (8):1087-1089 (1984), E. C. Munksgaard, M. Irie, and E. Asmussen, J. Dent. Res., 64 (12):1409-1411 (1985), U.S. Pat. Nos. 3,200,142, 4 259,075, 4,259,117, 4,368,043, 4,383,052, 4,443,197, 4,499,251, 4,537,940, and 4,539,382, and Danish Pat. Appl. No. 4898-83.

In addition, many phosphorus-based adhesives have been applied to dentin or enamel. Many of these adhesives have some degree of acidity and may, in some cases, cause mild etching of dentin or enamel. Examples of such adhesives include many of the phosphorus compounds described in the above-mentioned references, as well as those shown in U.S. Pat. Nos. 3,882,600, 3,997,504, 4,182,035, 4,222,780, 4,235,633, 4,404,150, 4,514,342, 4,515,930, 4,544,467, European Pat. No. 58483, European Published Pat. Appl. No. 0 155 812, and Japanese Laid-Open Pat. Appl. (Kokai) Nos. 57-14372 and 57-167364.

Many of the above-mentioned references stress that enhanced adhesion to dentin and/or protection from microleakage can be obtained if the pretreatment results in deposition of insoluble calcium salts on the surface of the dentin (see, e.g., U.S. Pat. No. 4,538,990).

U.S. Patent No. 4,380,432 describes a method for fixing prosthetic devices to teeth by etching the teeth with an etchant that preferably contains hydrochloric acid, followed by application of a methacrylate-based resin adhesive containing an elastomer. The compositions of the patent lack water and are not applied to dentin. The methacrylate-based adhesives exemplified in the patent are not water-soluble.

A reference of collateral interest to the instant invention, although not itself dealing with the priming of hard tissue, is U.S. Pat. No. 4,525,511. It describes a primer for high solids enamel automotive finishes.

Summary of the Invention

The present invention departs in several respects from some of the assumptions that have been made regarding hard tissue adhesives. The invention provides a pretreatment (a primer) that is applied directly to the dentin. When applied to dentin, it may cause etching of the dentin, but

avoids formation of substantial quantities of insoluble calcium salts on the surface of the dentin. The primer enables formation of extremely strong bonds to dentin, exhibiting shear strengths as high as 250 kg/cm², when tested in shear using the procedure shown in Example 1 of the aforementioned European Patent No. 58483. Many of the fractured samples fail cohesively within the composite button used in the shear strength test, indicating that the actual strength of the bond to dentin may be even higher than the measured value. Based on work previously carried out in the laboratory of the assignee of this invention, it had been assumed that the cohesive strength of dentin was approximately 100 kg/cm². Thus the present invention appears to reinforce dentin. Tests to date indicate that an extremely durable adhesive bond with little or no detectable microleakage can be obtained. The primers of the invention can, if desired, be water-based, thus substantially reducing the need to apply them in a dry field.

The present invention provides for the use of an acid and a water-soluble, polymerizable film former, for the manufacture of a polymerizable primer for coating dentin, wherein the acid and the film former are for application sequentially, said acid being applied before said film former, said acid having a pK_a less than or equal to that of phenol, said acid being rinsed from dentin and having a calcium salt which is soluble to form a homogeneous solution in water, said acid having a calcium salt which is insoluble in said film former, said film former being free of adhesively detrimental quantities of calcium salts that are not soluble in said film former.

In a further aspect the invention provides a kit for use in a method of preparing a primer for adhering to dentin, characterized in that said kit comprises an acid and a film former, wherein said acid and said film former are as described above, and wherein the kit components avoid formation of adhesively detrimental quantities of calcium salts that are not soluble in the film former, wherein the application of said acid, said film former and a dental restorative to dentin provides a bond with an average measured shear strength of at least 70 Kg/cm².

Detailed Description

In the practice of the present invention, the hard tissue which is adhered to or coated is dentin.

The acid and film former are applied to the dentin sequentially. The acid is rinsed from the dentin using a water rinse before application of the film former. For brevity, the acid and film former will sometimes be referred to collectively as the "primer".

The residual film is preferably overcoated with a layer of additional film former (the additional film former can be water-soluble or water-insoluble but should form a homogeneous solution when combined with the residual film), and then the additional film former and residual film are hardened and optionally overcoated with a composite or restorative (hereafter such composites and restoratives will be referred to collectively as "restoratives") or other hardenable coating. Thus the invention enables priming of dentin in order to improve the bond strength or durability of a restorative or coating applied thereto.

Acids for use in the present invention can be inorganic or organic acids, and if organic can be monomeric, oligomeric or polymeric. If desired, a precursor to the acid such as an acid anhydride, acid halide (including inorganic acid halides such as Lewis acids and organic acid halides), or ester can be used in place of the acid itself, e.g., to generate the desired acid *in situ*. Suitable acids include mineral acids, carboxylic acids, sulfonic acids, and phenols, with carboxylic acids, alkylsulfonic acids, and arylsulfonic acids being preferred.

The film former, when lying atop the dentin, should be sufficiently free of insoluble calcium salts so that if it is evaluated for shear bond strength according to the procedure of Reference Example 1 below, the bond should have an average measured shear strength of at least 70 kg/cm², more preferably at least 120 kg/cm².

The acid has a pK_a in water that is less than or equal to that of phenol, but the acid is soluble in the film former. The calcium salts, (or salts if the acid is polybasic) are however not soluble in the film former. Preferably, the pK_a of the acid is between +10 and -10, more preferably between -7 and +5. A "soluble" acid or calcium salt of an acid, is an acid or salt that when mixed with the film former (including any optional cosolvents that are present in the film former) under the desired conditions of use dissolves to form a homogeneous liquid mixture. Such conditions of use include temperature (e.g., body temperature), time (e.g., "standing time", that is, the amount of time the primer is allowed to remain on the surface of the dentin before hardening of the film former), and concentration. An evaluation of the solubility of the acid in the film former can be approximated by observing whether or not a homogeneous solution is formed when the acid is added to pure water, in an amount equivalent to the desired concentration of the acid in the film former. The solubility of the calcium salt(s) of the acid can be similarly approximated by adding slightly less than a stoichiometric amount of a suitable calcium compound (e.g., calcium carbonate) to the resulting acid solution, and observing whether or not a precipitate is formed.

Some degree of insolubility of the acid can be tolerated, but this appears to be detrimental to adhesion. The acid should be sufficiently soluble in the film former to provide the desired degree of adhesion on dentin. The degree of adhesion preferably is sufficient to provide an average measured shear strength at least 70 kg/cm², and more preferably at least 120 kg/cm², when evaluated using the procedure of Reference Example 1 below.

The acid can be liquid or a solid; if a solid it should be dissolved in a suitable solvent to enable the acid to wet the dentin. Liquid acids can also be dissolved in a suitable solvent, e.g., in order to facilitate wetting. Preferred solvents for the acid are the film former cosolvents discussed in more detail below.

The film former is a water-soluble liquid substance or water-soluble liquid mixture of substances, such substance(s) being organic monomers, oligomers, or polymers, being different from the acid, and being capable of forming a hardenable (e.g., polymerizable) continuous or semi-continuous film on the surface of the dentin. As used herein, a "water-soluble" film former has a water solubility (exclusive of any water that may be present in the film former) of at least 5 weight percent. Most preferably, the film former can be mixed with water in all proportions. Preferred film formers contain one or more substances having a sufficient number of water-solubilizing groups such as hydroxyl groups, carboxyl groups, sulfonic acid groups cationic salts (e.g., ammonium, phosphonium or sulfonium groups), amide linkages or polyether linkages to render the film former water-soluble. The film former preferably wets the dentin and most preferably has a sufficiently low viscosity to enable it to flow into interstices that already exist in the surface of the tissue or that are created therein by the action of the acid. To assist in hardening the film former, it preferably contains one or more polymerizable substances. Additional polymerizable substances (e.g., vinyl compounds such as acrylates and methacrylates) are especially preferred. The film former can also contain appropriate polymerization catalysts to assist in hardening the film former.

Preferred film formers include 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate ("HEMA"), 2- and 3-hydroxypropylacrylate and methacrylate, 1,3- and 2,3-dihydroxypropylacrylate and methacrylate, 2-hydroxypropyl-1,3-diacrylate and dimethacrylate, 3-hydroxypropyl-1,2-diacrylate and dimethylacrylate, pentaerythritol diacrylate and dimethacrylate, acrylic acid, methacrylic acid, 2-trimethylammonium ethylmethacrylic chloride, 2-acrylamido-2-methylpropanesulfonic acid, acrylamide, methacrylamide, 2-hydroxyethylacrylamide and methacrylamide, N,N-bis(2-

5 hydroxyethyl)acrylamide and methacrylamide, N-alkyl-N-hydroxyethyl acrylamides and methacrylamides, 2-and 3-hydroxypropylacrylamide and methacrylamide, methacrylamindopropyltrimethylammonium chloride, polyethyleneglycol (400) diacrylate and dimethacrylate, and mixtures thereof.

10 If the film former is a liquid mixture of substances, then the mixture preferably includes one or more suitable cosolvents. The cosolvent(s) aid in wetting the dentin and in solubilizing the acid. Suitable cosolvents include water, alcohols such as methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol, ketones such as acetone and methyl ethyl ketone, aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, acrolein, glutaraldehyde and 2-hydroxy-adipaldehyde, amides such as acetamide, and other substances such as tetrahydrofuran and dimethyl sulfoxide. The film former preferably contains less than 95 weight percent cosolvent, more preferably between 15 and 85 weight percent cosolvent.

15 The primer preferably contains only acid and film former. However, if desired other adjuvants such as polymerization catalysts, fluoride compounds, indicators, dyes, wetting agents, buffering agents, and thixotropes can be included in the primer, contingent upon attainment of the desired degree of bonding performance and suitability for use on the dentin.

20 Dentin to which the primer is applied preferably is first cleaned using conventional methods (e.g., by abrading it with a bur), rinsed (e.g., using water) and dried (e.g., using air). If desired, deep excavations in teeth can be lined with a conventional basing material, (e.g., calcium hydroxide or a glass ionomer cement).

25 As mentioned above, the film former preferably is overcoated with an optional layer of additional water-soluble or water-insoluble film former, and then hardened. Preferably, such additional film former is copolymerizable with the residual film formed by removal of volatile cosolvents from the primer, and contains a polymerization catalyst (preferably a photoinitiator) capable of hardening the residual film and additional film former. If desired, the additional film former can contain conventional fillers, and can also contain adjuvants of the type described above. A particularly preferred additional film former is obtained by combining the dimethacrylate derived from the reaction between methacrylic acid and the diglycidyl ether of bisphenol A ("Bis-GMA") with a hydrophilic monomer such as HEMA, hydroxypropyl methacrylate, or methacrylic acid. Additional monomers that can be combined with Bis-GMA include tetrahydrofuran methacrylate, glycidyl-1,3-dimethacrylate, triethyleneglycol dimethacrylate, ethyl

methacrylate, n-hexyl methacrylate, polyethyleneglycol dimethacrylate, and 1,6-hexanediol dimethacrylate. The additional film former can also contain cosolvents of the type described above.

Polymerization catalysts that can be included in the primer or in the additional film former are autocure or light cure catalysts such as those mentioned in columns 28 and 29 of U.S. Pat. No. 4,539,382, chromophore-substituted halomethyl-triazines such as those shown in U.S. Pat. No. 3,954,475, and chromophore-substituted halomethyl-oxadiazoles such as those shown in U.S. Pat. No. 4,212,970.

As also mentioned above, the primer and optional additional film former preferably are overcoated with a conventional restorative or coating. The dentin can then be finished using conventional techniques. For example, the primer can be overcoated with a dental adhesive and dental restorative and used, for example, to restore teeth, to install crowns, bridgework or other prosthetic devices, to seal pits and fissures or to veneer dentin.

Adhesion to dentin or enamel of various primers was evaluated as follows:

Five bovine teeth of similar age and appearance were partially embedded in circular acrylic discs. The exposed portion of each tooth was ground flat and parallel to the acrylic disc using Grade 120 silicon carbide paper-backed abrasive mounted on a lapidary wheel, in order to expose the dentin or enamel. During this and subsequent grinding and polishing steps, the teeth were continuously rinsed with water. Further grinding and polishing of the teeth was carried out by mounting Grade 320 silicon carbide paper-backed abrasive and then Grade 600 silicon carbide paper-backed abrasive on the lapidary wheel. The polished teeth were stored in distilled water, and used for testing within 2 hours after polishing. The polished teeth were removed from the water and dried using a stream of compressed air. A single drop of primer composition (containing varying amounts of acid, film former and optional water) was painted onto each of the polished tooth surfaces with a brush and allowed to stand for 60 seconds. The primer was then blown dry with compressed air and overcoated with a layer of additional film former. The overcoat was applied with a brush, blown lightly into a film with compressed air and cured using a 20-second irradiation with a "Visilux" dental curing light. Previously prepared molds made from a 2-mm thick "Teflon" sheet with a 4- or 5-mm diameter hole through the sheet were clamped to each polished tooth so that the central axis of the hole in the mold was normal to the polished tooth surface. The hole in each mold was filled with a visible light-curable dental restorative (typically "Silux"

brand restorative, universal shade, commercially available from 3M). ("Silux" is a trademark). The teeth and molds were allowed to stand for about 5 minutes at room temperature, then stored in distilled water at 37°C for 24 hours. The molds were then carefully removed from the teeth, leaving a molded button of restorative attached to each tooth.

Adhesive strength was evaluated by mounting the acrylic disk in a holder clamped in the jaws of an "Instron" apparatus with the polished tooth surface oriented parallel to the direction of pull. A loop of orthodontic wire (0.44 mm diameter) was placed around the restorative button adjacent to the polished tooth surface. The ends of the orthodontic wire were clamped in the pulling jaw of the Instron apparatus, thereby placing the bond in shear stress. The bond was stressed until it (or the dentin or button) failed, using a crosshead speed of 2 mm/min.

Claims

1. Use of an acid and a water-soluble, polymerizable film former, for the manufacture of a polymerizable primer for coating dentin, wherein the acid and the film former are for application sequentially, said acid being applied before said film former, said acid having a pK_a less than or equal to that of phenol, said acid being rinsed from dentin and having a calcium salt which is soluble to form a homogeneous solution in water, said acid having a calcium salt which is insoluble in said film former, said film former being free of adhesively detrimental quantities of calcium salts that are not soluble in said film former.
2. The use of claim 1 characterized in that said polymerizable film former contains one or more substances having a sufficient number of water-solubilizing groups to render said film former, exclusive of any water that may be present therein, soluble in water to at least 5 weight percent, said water-solubilizing groups being selected from hydroxyl groups, carboxyl groups, sulfonic acid groups, cationic salts, amide linkages and polyether linkages.
3. The use according to any preceding claim characterized in that said polymerizable film former contains one or more addition-polymerizable substances having one or more hydroxyl groups, carboxyl groups or sulfonic acid groups.
4. The use according to any preceding claim characterized in that said film former comprises a mixture of 2-hydroxyethylmethacrylate

and water.

5. The use according to any preceding claim characterized in that said polymerizable film former comprises at least one cosolvent selected from water, methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-2-propanol, acetone, methyl ethyl ketone, formaldehyde, acetaldehyde, propionaldehyde, acrolein, glutaraldehyde, 2-hydroxy-adipaldehyde, acetamide, tetrahydrofuran and dimethyl sulfoxide.
10. The use according to any preceding claim wherein an additional polymerizable film former is provided as an overcoating, said additional film former being hardenable using an auto-curing or light-curing polymerization catalyst.
15. The use according to preceding claim 6 characterized in that said additional film former forms a homogeneous solution when combined with said film atop dentin.
20. The use according to any one of preceding claims 6 and 7 characterized in that said additional film former comprises a copolymerizable mixture of diglycidal ether of bisphenol A (Bis-GMA) and a hydrophilic monomer selected from 2-hydroxyethylmethacrylate, hydroxypropylmethacrylate and methacrylic acid, and said polymerization catalyst comprises a photoinitiator.
25. A kit for use in a method of preparing a primer for adhering to dentin, characterized in that said kit comprises an acid and a film former, wherein said acid and said film former are as described in preceding claim 1, and wherein the kit components avoid formation of adhesively detrimental quantities of calcium salts that are not soluble in the film former, wherein the application of said acid, said film former and a dental restorative to dentin provides a bond with an average measured shear strength of at least 70 Kg/cm².
30. A kit according to claim 9, characterized in that application of the acid, the film former and a dental restorative to dentin provides a bond with an average measured shear strength of at least 120 Kg/cm².
35. A kit according to either of claims 9 and 10, characterized in that the acid and film former are not contained in the same composition.

**Claims for the following Contracting States :
AT, ES**

5. Use in a method of preparing a polymerizable primer for coating dentin of an acid and a water-soluble, polymerizable film former, wherein the acid and the film former are for application sequentially, said acid being applied before said film former, said acid having a pK_a less than or equal to that of phenol, said acid being rinsed from dentin and having a calcium salt which is soluble to form a homogeneous solution in water, said acid having a calcium salt which is insoluble in said film former, said film former being free of adhesively detrimental quantities of calcium salts that are not soluble in said film former.
10. The use of claim 1 characterized in that said polymerizable film former contains one or more substances having a sufficient number of water-solubilizing groups to render said film former, exclusive of any water that may be present therein, soluble in water to at least 5 weight percent, said water-solubilizing groups being selected from hydroxyl groups, carboxyl groups, sulfonic acid groups, cationic salts, amide linkages and polyether linkages.
15. The use according to any preceding claim characterized in that said polymerizable film former contains one or more addition-polymerizable substances having one or more hydroxyl groups, carboxyl groups or sulfonic acid groups.
20. The use according to any preceding claim characterized in that said film former comprises a mixture of 2-hydroxyethylmethacrylate and water.
25. The use according to any preceding claim characterized in that said polymerizable film former comprises at least one cosolvent selected from water, methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-2-propanol, acetone, methyl ethyl ketone, formaldehyde, acetaldehyde, propionaldehyde, acrolein, glutaraldehyde, 2-hydroxy-adipaldehyde, acetamide, tetrahydrofuran and dimethyl sulfoxide.
30. The use according to any preceding claim wherein an additional polymerizable film former is provided as an overcoating, said additional film former being hardenable using an auto-curing or light-curing polymerization catalyst.

7. The use according to preceding claim 6 characterized in that said additional film former forms a homogeneous solution when combined with said film atop dentin.

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8. The use according to any one of preceding claims 6 and 7 characterized in that said additional film former comprises a copolymerizable mixture of diglycidal ether of bisphenol A (Bis-GMA) and a hydrophilic monomer selected from 2-hydroxyethylmethacrylate, hydroxypropylmethacrylate and methacrylic acid, and said polymerization catalyst comprises a photoinitiator.

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9. A kit for use in a method of preparing a primer for adhering to dentin, characterized in that said kit comprises an acid and a film former, wherein said acid and said film former are as described in preceding claim 1, and wherein the kit components avoid formation of adhesively detrimental quantities of calcium salts that are not soluble in the film former, wherein the application of said acid, said film former and a dental restorative to dentin provides a bond with an average measured shear strength of at least 70 Kg/cm².

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10. A kit according to claim 9, characterized in that application of the acid, the film former and a dental restorative to dentin provides a bond with an average measured shear strength of at least 120 Kg/cm².

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11. A kit according to either of claims 9 and 10, characterized in that the acid and film former are not contained in the same composition.

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⑯ Use of a composition for the manufacture of a primer for coating dentin.

⑯ Use of an acid and a water-soluble, polymerizable film former, for the manufacture of a polymerizable primer for coating dentin, wherein the acid and the film former are for application sequentially, said acid being applied before said film former, said acid having a pK_a less than or equal to that of phenol, said acid being rinsed from dentin and having a calcium salt which is soluble to form a homogeneous solution in water, said acid having a calcium salt which is insoluble in said film former, said film former being free of adhesively detrimental quantities of calcium salts that are not soluble in said film former.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 6241

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
P, X	US-A-4 645 456 (JAMES JACK L) 24 February 1987 * column 3, line 15 - line 55; claims; example 3 *	1-8	A61K6/08
X, P	PATENT ABSTRACTS OF JAPAN vol. 010 no. 383 (C-393) ,23 December 1986 & JP-A-61 176507 (KANEBO LTD) 8 August 1986, * abstract *	1-8	
X	US-A-4 380 432 (ORLOWSKI JAN A ET AL) 19 April 1983 * column 5, line 19 - column 6, line 35; claims *	1-8	
A	US-A-4 362 889 (BOWEN RAFAEL L) 7 December 1982 * column 7, line 63 - column 9, line 10; examples 3,4 *	1-8	
A	EP-A-0 103 420 (TOKUYAMA SODA KK) 21 March 1984 * claims *	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.)
A	US-A-4 224 023 (CHEUNG PETER P L) 23 September 1980 * the whole document *	9-11	A61K
<p>The present search report has been drawn up for all claims</p>			
Place of search THE HAGUE	Date of completion of the search 5 December 1994	Examiner COUSINS-VAN STEEN, G	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			